On the estimation of the Kauzmann temperature from relaxation data

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The well known WLF equation describing the relaxation behaviour of glass-forming liquids near the glass transition temperature has been rederived on the basis of Adam and Gibbs' excess entropy model, making use of a novel expression for the entropy of undercooled liquids. It has been shown that C_2 in the WLF equation is a nearly constant fraction of $(T_s - T_2)$, where T_s and T_2 are the reference and the Kauzmann temperatures, respectively. It is demonstrated that the values of T_2 obtained from the relaxation data agree well with those calculated from thermodynamic data. The arguments used provide an explanation for the universality of the WLF constant, C_2.

(Keywords: Kauzmann temperature; relaxation; WLF equation)

INTRODUCTION

Adam and Gibbs[1] correlated the temperature dependence of relaxation phenomena in glass-forming liquids with the configurational entropy (S_c) of polymer melts through the temperature dependence of the size of a cooperatively rearranging region. Their molecular kinetic theory can be visualized as a development of an earlier suggestion of Gibbs and DiMarzio[2] that difficulties in packing polymers in the undercooled liquid state also reflect difficulties in producing configurational changes. A major result of the Adam and Gibbs theory is a relation akin to the well known William–Landel–Ferry[3–5] (WLF) empirical equation for the ratio (a_T) of relaxation times (τ), $a_T = \tau(T)/\tau(T_s)$, at any temperature T and that at a reference temperature, T_s. The WLF equation has the form

$$-\log a_{T_s}(\mathrm{T}) = \frac{C_1(T - T_s)}{C_2 + (T - T_s)} \qquad (1)$$

where C_1 and C_2 can be held constant at 8.86 and 101.6 K for a large number of substances provided T_s is chosen appropriately. Changing the reference temperature from T_s to T_s' changes C_1 and C_2 in a correlated fashion to a new set of values C_1' and C_2'

$$C_1' = \frac{C_1 C_2}{C_2 - (T_s - T_s')} \qquad (2a)$$

and

$$C_2' = C_2 - (T_s - T_s') \qquad (2b)$$

On the basis of the assumption that the heat capacity of glass-forming liquids is independent of temperature above the glass transition temperature (T_g), Adam and Gibbs[1] showed that the constants C_1 and C_2 can be related to the heat capacity difference (ΔC_p^g) between the equilibrium melt and glass at T_g, the Kauzmann isoentropic temperature[6] T_2, the potential energy hindering the cooperative rearrangement per monomer segment ($\Delta\mu$), the configurational entropy at the reference temperature $\Delta S_c(T_s)$ and a critical configurational entropy S_c^*. Choosing T_s' as T_g they showed that $T_g/T_2 = 1.30 \pm 8.4\%$ and $T_g - T_2 = 55\,\mathrm{K} \pm 10.9\%$.

We have recently demonstrated[7] that an accurate description of the free energy difference between an undercooled melt and the corresponding crystalline state, ΔG, can be provided by an expression obtained by the use of a Taylor series expansion of ΔG around its value at the melting temperature, T_m. Accordingly, we have

$$\Delta G = \Delta G^m - \left[\frac{\partial \Delta G}{\partial T}\right]_{T_m} \Delta T + \frac{1}{2!}\left[\frac{\partial^2 \Delta G}{\partial T^2}\right]_{T_m} \Delta T^2 - \frac{1}{3!}\left[\frac{\partial^3 \Delta G}{\partial T^3}\right]_{T_m} \Delta T^3 + \ldots \qquad (3)$$

where $\Delta T = (T_m - T)$ represents the undercooling and all derivatives are taken at $T = T_m$ and constant pressure. Noting that $\Delta G^m = 0$ and using the appropriate

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thermodynamic parameters for the derivatives of ΔG, we obtain

$$\Delta G = \Delta S^{\mathrm{m}}\Delta T - \frac{\Delta C_{\mathrm{p}}^{\mathrm{m}}\Delta T^2}{2T_{\mathrm{m}}}\left(1 + \frac{\Delta T}{3T_{\mathrm{m}}} + \frac{\Delta T^2}{6T_{\mathrm{m}}^2} + \frac{\Delta T^3}{10T_{\mathrm{m}}^3} + \dots\right) + \left[\frac{\partial \Delta C_{\mathrm{p}}}{\partial T}\right]_{T_{\mathrm{m}}}\frac{\Delta T^3}{6T_{\mathrm{m}}}\left(1 + \frac{2\Delta T}{4T_{\mathrm{m}}} + \frac{3\Delta T^2}{10T_{\mathrm{m}}^2} + \dots\right) \tag{4}$$

where ΔS^{m} and $\Delta C_{\mathrm{p}}^{\mathrm{m}}$ are the entropy and heat capacity differences respectively between the equilibrium melt and the crystal at the melting point. Each of the series in the parentheses is a logarithmic series and can be summed to yield

$$\Delta G = \Delta S^{\mathrm{m}}\Delta T - \frac{\Delta C_{\mathrm{p}}^{\mathrm{m}}\Delta T^2}{T_{\mathrm{m}} + T} + \left[\frac{\partial \Delta C_{\mathrm{p}}}{\partial T}\right]_{T_{\mathrm{m}}}\frac{\Delta T^3}{(T_{\mathrm{m}} + T)} \tag{5}$$

While summing the series, where necessary the approximation

$$\ln(T_{\mathrm{m}}/T) = 2\Delta T/(T_{\mathrm{m}} + T) \tag{6}$$

has been used. When the temperature dependence of ΔC_{p} is small, the last term in (5) can be neglected. An expression for the total entropy difference between the undercooled liquid and the equilibrium solid can be derived from (5) and used in conjunction with the Adam and Gibbs model to show that the constants C_2 and C_2' (obtained with $T_{\mathrm{s}}' = T_{\mathrm{g}}$) yield the same value of T_2 as obtained from the thermodynamic data.

TEMPERATURE DEPENDENCE OF ΔS_{c}

According to the Adam and Gibbs model[1]

$$-\ln a_{T_{\mathrm{s}}}(T) = \frac{\Delta\mu S_{\mathrm{c}}^*}{k}\left(\frac{1}{T_{\mathrm{s}}\Delta S_{\mathrm{c}}(T_{\mathrm{s}})} - \frac{1}{T\Delta S_{\mathrm{c}}(T)}\right) \tag{7}$$

where k is the Boltzmann constant. In order to evaluate the shift factor $a_{T_{\mathrm{s}}}(T)$ and obtain C_1 and C_2 of the WLF equation, we have to determine the temperature dependence of ΔS_{c}. Towards this end, we use equation (5) in the following form for ΔG and obtain ΔS. These expressions are given by

$$\Delta G = \Delta S^{\mathrm{m}}\Delta T - \Delta C_{\mathrm{p}}^{\mathrm{m}}\frac{\Delta T^2}{T_{\mathrm{m}} + T} \tag{8}$$

and

$$\Delta S = \frac{-\mathrm{d}\Delta G}{\mathrm{d}T} = \Delta S^{\mathrm{m}} - \Delta C_{\mathrm{p}}^{\mathrm{m}}\left(\frac{4T_{\mathrm{m}}^2}{(T_{\mathrm{m}} + T)^2} - 1\right) \tag{9}$$

According to Kauzman[6], ΔS becomes zero at T_2. Hence we can eliminate ΔS_{m} and express ΔS by

$$\Delta S = \frac{4T_{\mathrm{m}}^2\Delta C_{\mathrm{p}}^{\mathrm{m}}}{(T_{\mathrm{m}} + T_2)^2}\,\frac{(2T_{\mathrm{m}} + T_2 + T)(T - T_2)}{(T_{\mathrm{m}} + T)^2} \tag{10}$$

In the analysis to follow we attribute the entire ΔS to the difference in configurational entropy between the melt and the glass. This is in conformity with the experimental finding that the heat capacities of a polymer in its crystalline and amorphous states are almost identical near the glass transition temperature[8,9]. Use of (7) and (10) enables us to express the shift factor by

$$-\ln a_{T_{\mathrm{s}}}(T) = \frac{\Delta\mu S_{\mathrm{c}}^*}{k}\,\frac{1}{T_{\mathrm{s}}\Delta S_{\mathrm{c}}(T_{\mathrm{s}})}\,\frac{T - T_{\mathrm{s}}}{D} \tag{11}$$

where

$$D = (T - T_{\mathrm{s}}) + (T_{\mathrm{s}} - T_2)\left(1 - \frac{1 - \frac{3}{2}T_2/(T_{\mathrm{m}} + T_2)}{1 + \frac{3}{2}[(T_{\mathrm{s}} - T_2)/(T_{\mathrm{m}} + T_2)] + T_{\mathrm{s}}/(T - T_2)}\right)$$

and where $\Delta S_{\mathrm{c}}(T_{\mathrm{s}})$ is the residual entropy in the system on going from T_2 to T_{s}. The shift factor for the use of T_{g} as the reference temperature, $\ln a_{T_{\mathrm{g}}}(T)$, can easily be obtained by replacing T_{s} by T_{g}. It may be noted that the coefficients of $(T_{\mathrm{s}} - T_2)$ and $(T_{\mathrm{g}} - T_2)$ in these expressions are weakly temperature-dependent. However, to recover equations (2a) and (2b) from (11), one must replace T in the coefficients of $(T_{\mathrm{s}} - T_2)$ and of $(T_{\mathrm{g}} - T_2)$ by T_{g} and T_{s}, respectively. This will enable us to express

$$-\ln a_{T_{\mathrm{s}}}(T) = \frac{C_1(T - T_{\mathrm{s}})}{(T - T_{\mathrm{s}}) + \alpha(T_{\mathrm{s}} - T_2)} \tag{12a}$$

and

$$-\ln a_{T_{\mathrm{g}}}(T) = \frac{C_1'(T - T_{\mathrm{g}})}{(T - T_{\mathrm{g}}) + \beta(T_{\mathrm{g}} - T_2)} \tag{12b}$$

where

$$\alpha = 1 - \frac{1 - \frac{3}{2}T_2/(T_{\mathrm{m}} + T_2)}{1 + \frac{3}{2}[(T_{\mathrm{s}} - T_2)/(T_{\mathrm{m}} + T_2)] + T_{\mathrm{s}}/(T_{\mathrm{g}} - T_2)} \tag{13a}$$

and

$$\beta = 1 - \frac{1 - \frac{3}{2}T_2/(T_{\mathrm{m}} + T_2)}{1 + \frac{3}{2}[(T_{\mathrm{g}} - T_2)/(T_{\mathrm{m}} + T_2)] + T_{\mathrm{g}}/(T_{\mathrm{s}} - T_2)} \tag{13b}$$

The WLF equation is generally valid in the range $T_{\mathrm{g}} \pm 50\,\mathrm{K}$. In this small interval of temperature, the change in the magnitude of the coefficient of $(T_{\mathrm{s}} - T_2)$ in the denominator of equation (11) is small. Hence replacing T in this coefficient by T_{s} or T_{g} yields an average value for the coefficient. Thus α and β can be treated as constants over the temperature range of validity of the WLF equation. It also follows that

$$C_1 = \frac{\Delta\mu S_{\mathrm{c}}^*}{k}\,\frac{1}{T_{\mathrm{s}}\Delta S_{\mathrm{c}}(T_{\mathrm{s}})} \tag{14a}$$

$$C_2 = \alpha(T_{\mathrm{s}} - T_2) \tag{14b}$$

$$C_1' = \frac{\Delta\mu S_{\mathrm{c}}^*}{k}\,\frac{1}{T_{\mathrm{g}}\Delta S_{\mathrm{c}}(T_{\mathrm{g}})} \tag{14c}$$

and

$$C_2' = \beta(T_{\mathrm{g}} - T_2) \tag{14d}$$

According to Kauzmann[6], when kinetic processes do not intervene, an undercooled liquid is forced to exhibit glass transition at T_2, the isoentropic temperature. Hence, it is reasonable to assume that ΔC_p attains its theoretical maximum at T_2. If so, a relationship between T_2 and T_m can be derived from (9) noting that

$$\Delta C_p = T\frac{\partial \Delta S}{\partial T} = 8\Delta C_p^m \frac{T_m^2 T}{(T_m + T)^3} \tag{15a}$$

and

$$\frac{\partial \Delta C_p}{\partial T} = 8\Delta C_p^m T_m^2 \frac{T_m - 2T}{(T_m + T)^4} \tag{15b}$$

The derivative in (15b) must vanish at $T = T_2$, if ΔC_p reaches its maximum value at this temperature. Equating (15b) to zero, we observe that $T_2/T_m = 0.5$. This has been found to be true for a large number of glass-forming liquids[10]. With this assumption, (13a) and (13b) can be further simplified to yield

$$\alpha = \frac{1}{1 + (T_2/T_s)(T_g - T_2)/(T_g + T_2)} \tag{16a}$$

and

$$\beta = \frac{1}{1 + (T_2/T_g)(T_s - T_2)/(T_s + T_2)} \tag{16b}$$

respectively.

In the literature, it is often shown[11-13] that $C_2' \equiv (T_g - T_\infty)$, where T_∞ is the characteristic temperature of the Vogel–Fulcher equation. In the framework of the free volume model of liquids, the Vogel–Fulcher equation is identical to the WLF equation only if the free volume with respect to that at the glass transition temperature is a linear function of T. This condition is not valid[5] below T_g. According to the present analysis, such an equivalence is possible only if $\beta = 1.0$. From (12b), it follows that $\beta = 1.0$ only at $T = T_2$. Our analysis, therefore, shows that to estimate T_2 correctly from experimental viscosity data obtained at temperatures above T_g, either α or β (depending on the reference temperature used) has to be incorporated in the WLF equation.

Since C_2 is universal, knowledge of T_s and T_g only enables the estimation of T_2 through (14b) and (16a). Values of T_2 for a number of polymers were obtained by this procedure with the aid of data compiled by William and coworkers[3-5] and are shown in *Table 1*. Values of T_g can also be derived from a knowledge of C_2' and T_g only. These are also presented in *Table 1*. According to the present model T_2 values derived from viscosity data should correspond to the value obtained from thermodynamic data. However, thermodynamic data are relatively scarce and we have attempted such a comparison with respect to only a few polymers. The results are shown in *Table 2*. In this analysis C_p was assumed to be linearly dependent on temperature. It may be noted that in all cases agreement between T_2 derived from viscosity or other relaxation data and that from thermodynamic data is excellent and far better than in the case of the Adam and Gibbs[1] evaluation.

It is also expected that T_2 values obtained from C_2 and C_2' should agree amongst themselves. However, we find that the agreement is not in general satisfactory. The

Table 1 Calculated values of T_2, α and β obtained on the basis of the experimental parameters T_s, T_g, C_2 and C_2'. Values of T_2, α and β in columns marked 'a' refer to the use of T_s, T_g and C_2 while those in columns marked 'b' were obtained from T_g, C_2' and C_2

Material	T_s (K)	T_g (K)	C_2' (K)	T_2 (K)		T_g/T_2		α		β	
				a	b	a	b	a	b	a	b
Polyisobutylene	243	202	80.0	126.6	107.0	1.559	1.887	0.896	0.872	0.837	0.842
Polystyrene	408	354	–	300.3	–	1.179	–	0.943	–	0.886	–
	–	373	50.0	–	316.8	–	1.177	–	0.943	–	0.890
Poly(vinyl acetate)	349	301	–	239.5	–	1.257	–	0.928	–	0.871	–
	–	305	46.8	–	251.4	–	1.213	–	0.937	–	0.873
Poly(vinyl chloroacetate)	346	296	40.4	236.7	249.6	1.251	1.186	0.930	0.944	0.870	0.870
Poly(methyl acrylate)	324	276	45.0	213.9	223.9	1.290	1.233	0.923	0.934	0.863	0.864
Poly(methyl methacrylate)	423	378	–	325.7	–	1.161	–	0.947	–	0.891	–
	–	381	80.0	–	291.2	–	1.308	–	0.912	–	0.891
Glucose	351	305	–	241.2	–	1.264	–	0.925	–	0.872	–
Propylene glycol	217	160	–	105.2	–	1.521	–	0.909	–	0.814	–
Butadiene–styrene, 75/25	268	212	–	157.6	–	1.351	–	0.920	–	0.834	–
	–	210	25.6	–	179.4	–	1.171	–	0.953	–	0.836
Glycerol	238	187	–	125.9	–	1.485	–	0.906	–	0.828	–
Hevea rubber	–	200	53.6	–	135.8	–	1.473	–	0.905	–	0.834
Polyethylene	–	231	73.2	–	144.8	–	1.595	–	0.886	–	0.854
Poly(propylene oxide)	–	198	24.0	–	169.1	–	1.171	–	0.954	–	0.830
Poly(α-methyl styrene)	–	445	49.3	–	390.5	–	1.140	–	0.951	–	0.905
Poly(hexene-1)	–	218	20.2	–	194.0	–	1.124	–	0.963	–	0.840
Ethylene–propylene	–	242	40.7	–	194.2	–	1.246	–	0.934	–	0.851
Cellulose tributyrate in dimethyl phthalate,											
21%	247	188	42.6	136.5	136.5	1.377	1.377	0.920	0.920	0.828	0.828
43%	–	193	38.6	–	146.4	–	1.318	–	0.897	–	0.828
Polyurethane	283	238	32.6	171.3	199.6	1.389	1.192	0.910	0.946	0.850	0.849
n-Butyl	–	300	96.6	–	189.1	–	1.586	–	0.877	–	0.871
Cellulose nitrate in diethyl phthalate, 23%	–	166	53.5	–	100.8	–	1.647	–	0.897	–	0.821
Average						1.340 ±12.5%	1.36 ±21%	0.921 ±1.4%	0.924 ±2.8%	0.854 ±2.4%	0.854 ±2.4%

Table 2 The Kauzmann temperature T_2 calculated from thermodynamic data on the basis of a linear dependence $\Delta C_p = a + bT$ (T_2^{calc}), from relaxation data using (14) and (16) (T_2^{η}), from Adam and Gibbs' expression using constant ΔC_p at T_g (T_2^{AG}), and with the aid of the conventional WLF equation (T_2^{WLF})

Material	Ref.	a (J mol^{-1} K^{-1})	b (J mol^{-1} K^{-1})	ΔS^{m} (J mol^{-1} K^{-1})	T_g (K)	T_m (K)	T_2^{calc} (K)	T_2^{η} (K)	T_2^{AG} (K)	T_2^{WLF} (K)
Polyethylene	9	35.274	−0.0714	18.0	231	414	143.9	144.8	158.8	157.8
Hevea rubber	9	55.393	−0.1389	23.0	200	421	132.8	135.8	171.2	146.4
Polystyrene	9, 14	102.647	−0.1767	17.56	354	513	299.3	300.3	331.1	306.4
Poly(propylene oxide)	9	62.390	−0.1154	23.9	198	348	171.0	169.1	190.1	174.0

reason is not hard to see. Very often experimental data are not in agreement with (2b). Our analysis demands satisfaction of (2b). Further when data are analysed and fitted to the WLF equation with different reference temperatures (T_s and T_g in the present case) the fits need not be equally good, leading to a violation of (2b). Where (2b) is satisfied reasonably well, we get better agreement between the two T_2 values.

Table 1 also shows the values of α and β arising out of the T_2 values obtained in the present analysis. It is remarkable that α and β are virtually constant for the large number of polymers analysed. Their average values derived from either method of analysis are identical and equal to $0.921 \pm 1.4\%$ and $0.854 \pm 2.4\%$ respectively. The constancy of α and β implies that T_g/T_2 and T_s/T_2 vary in a correlated fashion. With the aid of α and β one can show that

$$T_s - T_g = \frac{1}{1-\beta}\frac{\alpha-\beta}{\alpha}C_2 \qquad (17)$$

The average values of α and β yield $T_s - T_g = 50.6$ K. These findings together with the constancy of the product C_1C_2 explain why the WLF equation is so successful as a generalization.

CONCLUSIONS

Consideration of a novel expression for the temperature dependence of the entropy of undercooled liquids with respect to the equilibrium solid (ΔS) and the Adam and Gibbs excess entropy model for the cooperative relaxation properties of glass-forming liquids is shown to yield the well known WLF equation. The magnitude of ΔS is derived from an expression for the corresponding ΔG for the liquid obtained by a Taylor series expansion of ΔG around T_m. It is observed that the values of the Kauzmann temperature T_2 obtained by a reinterpretation of the values of C_2 and C_2' in the WLF equation agree with those derived from experimental thermodynamic data. The results also explain broadly the reasons for the universality of WLF constants.

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